Efficacy of Hindered Amines in Woodflour-Polypropylene Composites Compatibilized with Vinyltrimethoxysilane After Accelerated Weathering and Moisture Absorption

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ABSTRACT: In this work, the aim was to analyze the efficacy of hindered amine light stabilizers (HALS) in wood-flour-polypropylene composites compatibilized with vinyl-trimethoxysilane after moisture absorption and accelerated weathering. Moisture uptake of materials decreased with incorporation of silane due to diminished accessibility of water molecules to reactive regions. In dynamic mechanical experiments performed on wet samples, a marked reduction in the storage modulus in the glassy and rubbery zone was observed, since water has a plasticizing effect. After sample weathering, in a xenon-arc apparatus, the changes in chemical structure and physical properties after exposure were analyzed by attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy, color measurement, flexural properties, and morphological analysis by scanning electron microscopy (SEM). The data showed that HALS maintain the brightness of the materials after aging and prevent sample whitening. They also reduced color loss after aging and the SEM micrographs revealed that they inhibit surface cracking during weathering. Although a slight decline in the mechanical properties was not completely avoided, the combination of the additives studied (UV absorbers and HALS) successfully prevented the deterioration of surface materials by UV radiation. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 2017–2026, 2011

Key words: composites; compatibilization; HALS; radiation; polyolefin

INTRODUCTION

The introduction of wood plastic composites (WPC) in construction (indoor and outdoor) and automotive applications are mainly responsible for the growth in the fabrication and application of wood flour/plastic composites in recent years.

The reinforcement of thermoplastic materials with wood derivatives represents an alternative to inorganic fillers. The increased interest in the use of woodflour as filler in thermoplastics is due to its many advantages.[1] Low density, high strength and stiffness, and low price are some of these advantages.[2–4] Furthermore, it does not cause abrasion in the extruder screws during processing and it produces a smaller ecological impact compared with the mineral fillers.[5]

The main drawback of the use of wood as reinforcement in thermoplastics is in achieving strong interfacial adhesion between the hydrophilic surface of the wood and the hydrophobic thermoplastic polymers. Hence, generally this kind of polymeric system has poor mechanical properties.[6,7] The properties of WPCs can be improved by optimizing the interface between the matrix and the filler, i.e., using coupling as maleated polypropylene (MAPP).[8–13] Recently, the use of a new organosilane as coupling agent for WPCs has received considerable attention due to its effectiveness in stabilizing the chemical bonds between the wood particles and several thermoplastic matrices.[14–16] Specifically, the silane is incorporated into the formulation in small amounts, less than 2%, unlike maleic.

The lifetime of composites depends on several factors, such as polymer structure, history of the thermoplastic (virgin, recycled), presence of fillers, moisture, antioxidants and their amounts, processing conditions,[17] density, or weathering.[18] The use of these materials for outdoor applications requires a study of the environmental effects on the properties of the composites, to estimate durability. Weathering

produces loss of the mechanical properties[19–21] or color change,[22–24] because WPCs tend to lighten over time.[25] To prevent multiple environmental factors from shortening the lifetime of WPCs, the commercial woodflour-plastic composites usually contain added antioxidants.

The low water absorption of WPCs compared with that of wood is one of the most remarkable features of composite materials. However, moisture absorption contributes to a whitening effect, given water accelerates oxidation reactions.[26]

The photostabilizers incorporated into the polypropylene matrix, UV absorber, and HALS (hindered amine light stabilizers) can reduce the lightness of the composite material, but act in different ways. Thus, the UV absorber reduces lightening because it absorbs UV radiation, and as a result, the material gets less radiation and the bleaching of wood is lower. Moreover, the addition of HALS blocks the absorption of UV radiation.

It is intended that the materials designed in this article maintain good dimensional stability when exposed to the environment. After selecting the silane coupling agent to link wood and thermoplastic matrix is necessary to include additives that prevent the harmful effects of exposure to environmental agents. Several studies examined the behavior of wood that has been degraded by various factors[27] as well as the degradation of polypropylene.[28] There are also papers in the literature that study the deterioration by weathering trial, without specific additives or zinc ferrites.[23,29] Also studies have been conducted in which assesses the performance of composite materials of polyethylene/wood flour and maleated polypropylene with HALS.[22] However, there are no studies that focus on polypropylene composite materials and wood flour treated with a silane coupling agent and a combination of antioxidants and hindered amines, with the aim of prevent the negative effects of radiation exposure, humidity, and/or temperature. The use of silane and additives mentioned earlier is done in small amounts, thus maintaining the initial advantage of low-cost end of these materials. Thus, obtained materials maintain their initial mechanical and thermal properties, and that also protects against radiation because of it was reported that HALS function as a spin-trapping agent.[30]

The objective of this work is to study the influence of vinyltrimethoxysilane and photostabilizers on the new polypropylene-woodflour composites, when these materials remain in humid environment and accelerated weathering.

The methodology used to achieve these objectives has been structured in different phases as follows: the search and selection of woodflour, thermoplastic materials and coupling agent, processing of reinforced compounds, and physic–chemical characterization of the new WPCs. To determine the change in the chemical structure, the materials were analyzed by attenuated total reflectance and by scanning electron microscopy.[31–33]

EXPERIMENTAL

Materials

The raw material used to prepare the woodflour composites was an isotactic polypropylene PP (ISPLEN® PP 070 G2M), provided by RepsolYPF, with a density of 0.902 g cm^{-3} and a melt flow index of 10 g/10 min (230°C/2.16 kg). A woodflour (WF) from red pine provided by Maderas del Noroeste S.A., Spain was used as filler. Because woodflour particle size can affect the mechanical properties of the composite, the WF was separated using an automatic vibratory sieve shaker to obtain WF particles of similar sizes. Only particles that passed through a sieve of mesh 400 μm were used in this study.

The coupling agent used was Geniosil XL 10, which corresponds to a vinyltrimethoxysilane, provided by Wacker. From the conclusions of a previous paper,[21] the amount of vinyltrimethoxysilane used was ∼ 1% (w/w) with respect to the woodflour mass.

The UV absorber used was 1% TINUVIN® 326 with 0.6% of hindered amine stabilizer (TINUVIN® 791) in combination with 0.2% IRGANOX® B 225 for the best results. All stabilizers were supplied by Ciba Specialty Chemicals.

Finally, an alkene bis fatty amide (Glycolube WP2200), provided by Lonza Group, was added to the formulation as processing aid with a proportion of 3% with respect to the blend mass. These amounts were selected following the advice of the different suppliers.

Sample preparation

Before the extrusion process, the woodflour was dried for 24 h at 100°C until 0.5–1% moisture content was reached to prevent steaming in the extruder. The drying of the woodflour before processing is an important step, since moisture acts as a separating agent in the filler–matrix interface.[34] The thermogravimetric tests performed showed that the woodflour did not suffer thermal degradation during the drying process.[31,32,35] A twin screw extruder (DSE 20 Brabender) was used for the preparation of the composites. The temperatures of the barrel and the die were maintained at 190°C during the extrusion and the screw rate was 45 rpm. The extrudate was cooled and pelletized at the die exit. Then, the pellets were dried and injection molded into standard

specimens according to ISO 178 using a Battenfeld Plus 350, with an injection pressure of 1400 bar, a barrel temperature of 180°C, and an injection rate of 56 cm^3 s^{-1}.

For the woodflour treated with vinyltrimethoxysilane, the silane was added in water by means of standard mixing methods (high-speed stirrer), after the solution was mixed into the woodflour and finally dried at 100°C for 24 h before composite extrusion.

The nomenclature used for the different polymer-woodflour composites was as follows:

a. Polypropylene-untreated woodflour: A, C, and E with 10, 30, and 50% woodflour mass, respectively.
b. Polypropylene-silane treated woodflour: silane percentage was indicated in all cases, i.e., A1 corresponds to the WPC with 10 wt % woodflour treated with 1 wt % silane.
c. Polypropylene-woodflour-light stabilizers: designated with HALS subscript, i.e., A1$_{HALS}$.

Moisture absorption

WPC samples (20 mm × 4 mm × 2 mm parallelepipeds) were used for the absorption experiments. Relative humidity (RH) was established using a water bath (100% RH) at room temperature (25°C). Moisture absorption at any time t (M_t) was defined by eq. (1).

$$M_t = \frac{M - M_0}{M_0} \times 100 \tag{1}$$

where M is the mass of the wet sample and M_0 is the mass of the dry sample. The samples were removed from the water bath and absorbent paper was used to dry the surface before they were weighed. The time needed for removing the sample, drying, weighing, and returning the sample to the recipient was less than 1 min for each sample. An analytical balance Sartotius YDK Serie Master^{pro} (0.1 mg precision) was used to weigh samples.

Dynamic mechanical analysis

The dynamic mechanical behavior of the samples was studied using a Perkin–Elmer DMA 7 analyzer. The samples were analyzed in the three-point bending mode. The tests were performed from −50 to 150°C, at a heating rate of 2°C/min under a flow of helium with a deformation frequency of 1 Hz. The storage modulus (E') and damping ratio (tan δ) were recorded as a function of the temperature to evaluate the WPC properties. The wet samples were analyzed after they reached equilibrium in the water bath.

Weathering exposure and surface analysis

The WPC samples according to ISO 179 were placed in a xenon arc-type light exposure apparatus (Xenotest Alpha LM-W). The samples were mounted in 10 rows on a drum that rotates around the xenon arc bulb. These samples were rotated periodically to ensure that all surfaces were exposed to the same irradiance. Finally, they were removed after 102.674 kJ m^2 of total irradiance and they were analyzed.

A Konica Minolta CM-2600d spectrophotometer was used to quantify color changes at the surfaces of WPCs after weathering. Color was expressed using the CIE Lab (L^*, a^*, and b^*) system. Color changes due to weathering, ΔE^*, and brightness (ΔL^*) were calculated from the L^*, a^*, and b^* values. The a^* coordinate represents the red–green direction, whereas b^* coordinate represents the yellow–blue direction. The total color change, ΔE, was calculated according to ASTM D2244 as seen in eq. (2).

$$\Delta E = \sqrt{\left(L_2^* - L_1^*\right)^2 + \left(a_2^* - a_1^*\right)^2 \left(b_2^* - b_1^*\right)^2} \tag{2}$$

where subscript 1 denotes the values before exposure and subscript 2 denotes the values after exposure. For each sample, color change was measured on five different specimens.

Mechanical properties

Flexural tests were performed at a crosshead speed of 2 mm min^{-1} and at room temperature using an Instron 5566 Universal Testing Machine (Instron, Canton, MA). The span length was 64 mm. At least eight specimens from each wood-polypropylene formulation were tested to obtain the average value of the mechanical parameters and their standard deviations.

FTIR/ATR analysis

Fourier transform infrared (FTIR) spectra of samples were obtained by an OPUS/IR PS15 spectrometer (Bruker) using attenuated total reflectance (ATR). The composite surfaces were in contact with the MKII Diamond top plate crystal at a 45° angle of incidence, with manual pressure. Background spectra were taken in the empty chamber to compensate for the moisture in the air around the tested samples. The spectra were the results of 100 scans at 4 cm^{-1} resolution between 400 and 4000 cm^{-1}.

Carbonyl and vinyl indexes and absorbed water content were calculated using eqs. (3) and (4), where the peak intensities at 2916, 1726, and 900

correspond to the C—H stretching vibrations, the carbonyl C=O and vinyl groups, respectively.

$$\text{Carbonyl index} = \frac{I_{1726}}{I_{2916}} \times 100 \qquad (3)$$

$$\text{Vinyl index} = \frac{I_{900}}{I_{2916}} \times 100 \qquad (4)$$

Scanning electron microscopy

A LEO-435VP (LEICA Microsystems, Cambridge, UK) scanning electron microscope (SEM) at an accelerating voltage of 8 kV was used to study the morphology of the composites. The uncoated surfaces were observed by SEM of variable pressure.

RESULTS AND DISCUSSION

Effect of moisture absorption

The isothermal absorption curves of WPC were studied as a function of woodflour content with and without silane treatment. Figure 1 shows that absorbed moisture increased with woodflour content as a function of exposure time. Equilibrium state was reached at different times for the different samples. The PP did not absorb any moisture[36] when exposed to the different test environments, indicating that moisture is absorbed by the hydrophilic component of the composite (woodflour) and not by the hydrophobic PP.[26] As expected, the material with the highest WF content without silane treatment (E sample) absorbed the most moisture, possibly caused by the gap and flaw at the interface between the filler particles and PP, which increases as a result of the poorer dispersion and wetability of woodflour.[20,26,29,37] The data of the water mass absorbed when the samples reached the saturation point ($M_{t(sat)}$) are summarized in Table I. Moisture absorption is mainly due to hydrogen bonding of water molecules to the hydroxyl groups on the cell wall of the wood. Theoretically, strong adhesion at
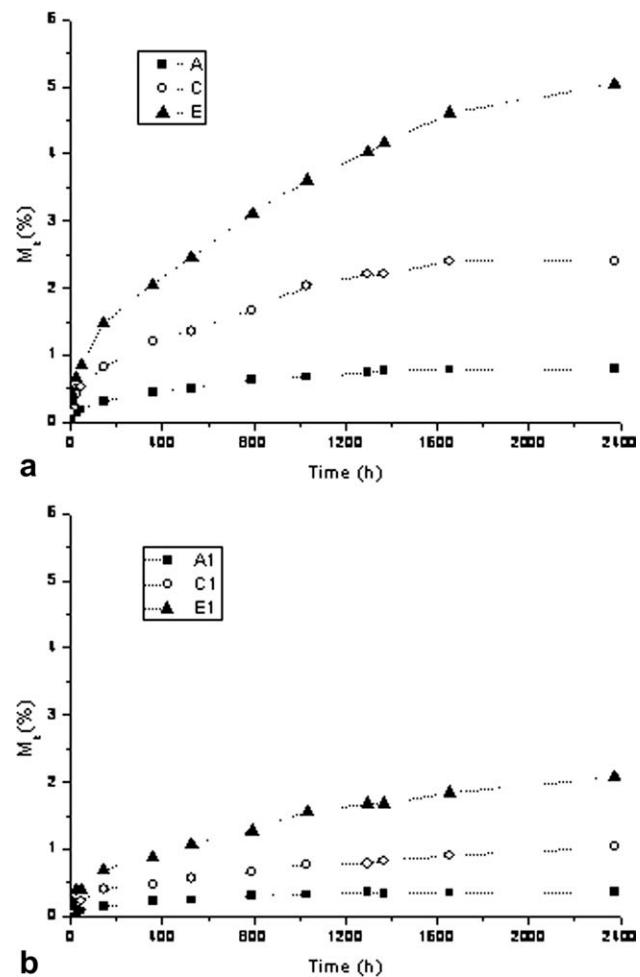

Figure 1 Water absorption versus time of the samples without silane (a) and with silane (b).

the filler–matrix interface can prevent the water from penetrating, taking into account that water absorption can be an indirect measurement of interface adhesion. Previous studies have shown that there is poor compatibility between the hydrophilic woodflour and hydrophobic polypropylene, hence, the weak interfacial adhesion.[31–33] After the wood was treated with the coupling agent, the physical

TABLE I
Storage Modulus, Loss Tangent Values, and Saturation Point (Mt(sat)) for the PP and Composites

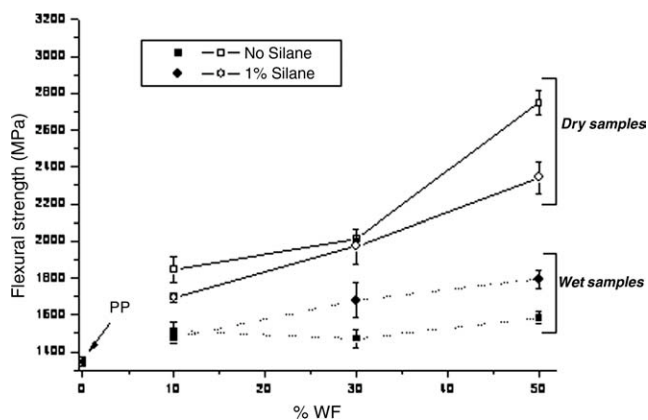|	Dry samples			Wet samples			
	E' (10^9 Pa)			E' (10^9 Pa)			
Sample code	$T = -30°C$	$T = 30°C$	T_g (°C)[a]	$T = -30°C$	$T = 30°C$	T_g (°C)[a]	$M_{t\,(sat)}$ (%)
PP	4.63	2.34	9.4	4.63	2.34	9.4	0
A	5.53	3.78	11.2	4.07	1.95	9.5	0.794
A1	4.51	2.54	9.7	4.73	1.08	9.5	0.364
C	5.87	3.84	10.0	4.74	3.39	8.9	2.403
C1	7.08	3.94	10.6	6.90	2.17	9.3	1.037
E	4.29	2.66	13.7	5.58	2.24	8.6	5.041
E1	4.69	2.90	9.9	3.47	1.91	8.6	2.071

[a]These values were measured in the tan δ curve.

Figure 2 Flexural modulus of WPC composites for the dry and wet samples.

properties of the WPC improved and the morphological studies proved that organosilane enhanced the filler dispersion into the matrix and the interface adhesion which were the principal causes of the improvement in the WPC properties. Figure 1(b) reveals that water absorption is lower for the composites containing coupling agent, this reduction being more than 50%, with respect to the samples without silane. Therefore, the use of a coupling agent can influence the moisture uptake of PP/woodflour composites.[20,38] This could be attributed to the lower amount of free OH in woodflour[39] and to the increase in the interface adhesion between the components. Silane can stabilize the bonds between woodflour and PP, which imparted hydrophobicity to the woodflour and improved the interfacial adhesion between woodflour and PP.[40] The gaps and flaws in the interface decreased, therefore, making it more difficult for the water molecules to penetrate into the composite. So, the water absorbed at saturation point was less than half that for the composites without coupling agent.

Dynamic mechanical analysis of wet samples

Table I shows the storage modulus (E') at different temperatures and the temperature of the glass transition (T_g) for the dry and wet samples. The dynamic mechanical experiments in the dry samples indicated that storage modulus in the glassy zone increased with woodflour amount up to a maximum value in sample C (30% woodflour). Storage modulus in the rubbery zone showed a more marked increase with woodflour amount; again, the maximum value was obtained for sample C.[32] If we compared these results with those of the wet samples, we can observe a reduction in the storage modulus and glass transition values for all the samples studied, except for sample E. The water in the structure has a plasticizing effect on the system. This can

be the principal cause of the stiffness diminution and why glass transition temperature was slightly lower for the wet samples than for the dry. This reduction is greater in samples without silane, because these samples soak up more humidity which can modify their interface due to the water incorporation.

Mechanical properties

Figure 2 shows the values of flexural modulus of composite materials based on the contents of filler and coupling agent, for dry and wet samples. In the dry samples, the modulus increases with the wood content, primarily due to the incorporation of rigid particles into the polypropylene matrix, this being observed in both composites with and without silane. Wood treatment with organosilane reduces the flexural modulus of the composites. As proven in a previous paper,[33] the coupling agent modifies the surface of the filler particles, hindering the PP molecules from filling the wood capillaries and consequently slightly decreasing composite stiffness.

In wet samples (Fig. 2), there was a drop in modulus, as expected. As a general rule, an increase in moisture content implies a decline in the modulus of the composites.[41] In fact, the absorption of moisture involves the formation of new hydrogen bridges between the cellulose and water molecules. This may deteriorate the interfacial adhesion, and as a result, produce a decrease in the flexural modulus.[42]

With the presence of silane in the formulations, the hydrophobic nature of the filler increases, and therefore, the decrease in the mechanical properties is smaller than in the samples without silane.

Figure 3 shows the flexural strength values for the dry and wet samples. It is important to stand out that they did not reach the break under the test conditions used.
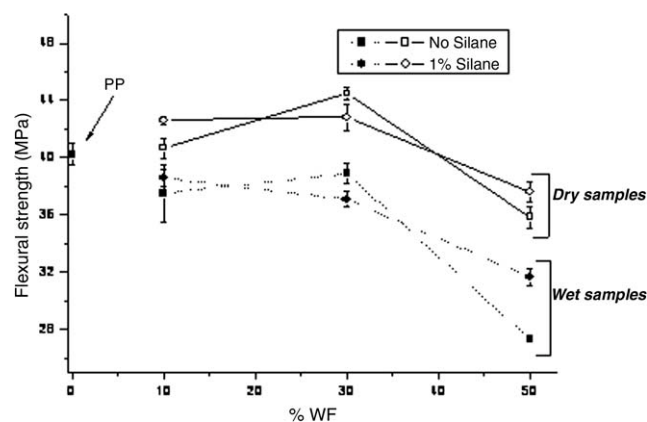

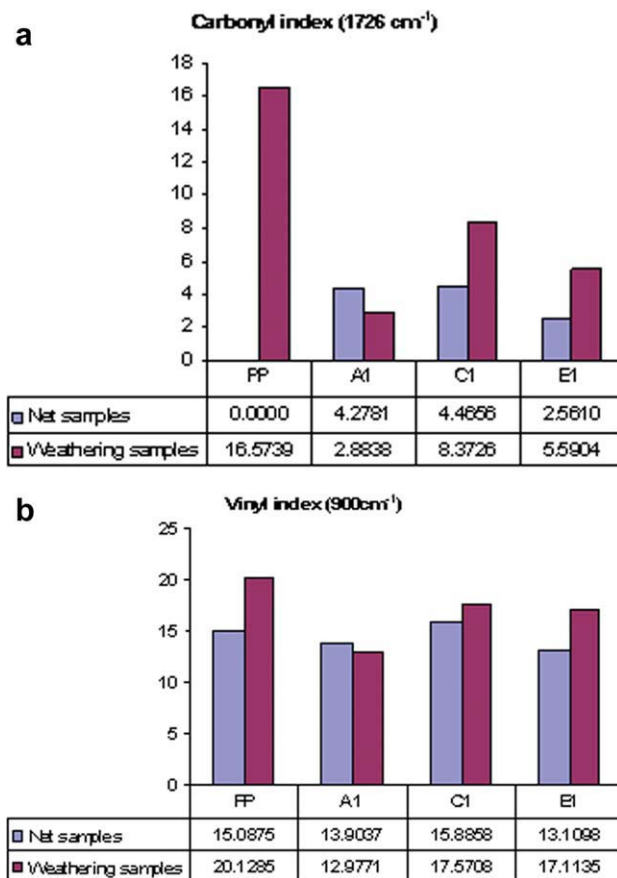**Figure 3** Flexural strength of WPC composites for the dry and wet samples.

Figure 4 Carbonyl index (a) and vinyl index (b) for the neat samples and weathered samples without HALS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

The flexural strength values, which depend on filler content, are kept almost constant to 30%, and decrease in the compositions with large amounts of filler, up to 37 MPa. The flexural strength of composite materials is influenced by the quality of the interface, which allows the transference of strength between matrix–filler. The coupling agent produces a stronger PP-wood interface, hence, allows the establishment of chemical bonds between the filler and the matrix, and consequently, improves the transference of strength between both of them. This phenomenon can be responsible for the flexural strength increase. However, it cannot explain the peculiarity of sample C that shows a different behavior. The effect observed is probably a combination of different competing mechanisms: on the one hand, the improvement of the interface, and on the other hand, the diminution of the material stiffness which allows matrix deformation with lower strength. In the wet samples, the interface is modified by water which acts as a plasticizer, affecting the filler and the interface, and as a result, modifies the mechanical behavior of composite materials.[42–44] Hence, the values of flexural strength diminished in

all the samples although the trend was similar to that in the dry samples.

Effect of radiation XENOTEST

To estimate the effects of weathering on the chemical structure of the composites, the carbonyl and vinyl indexes were measured[45] by FTIR/ATR spectrometry.

Moreover, the composites show a significant increase in the carbonyl index [Fig. 4(a)] after weathering, indicating that an increase in the carboxylic acid derived mainly from lignin degradation.[46] The carbonyl formation indicated that surface oxidation occurred. The vinyl index [Fig. 4(b)] remained relatively constant after weathering. The formation of terminal vinyl groups indicated that photodegradation occurred via Norrish II reactions, resulting in chain scission.[47]

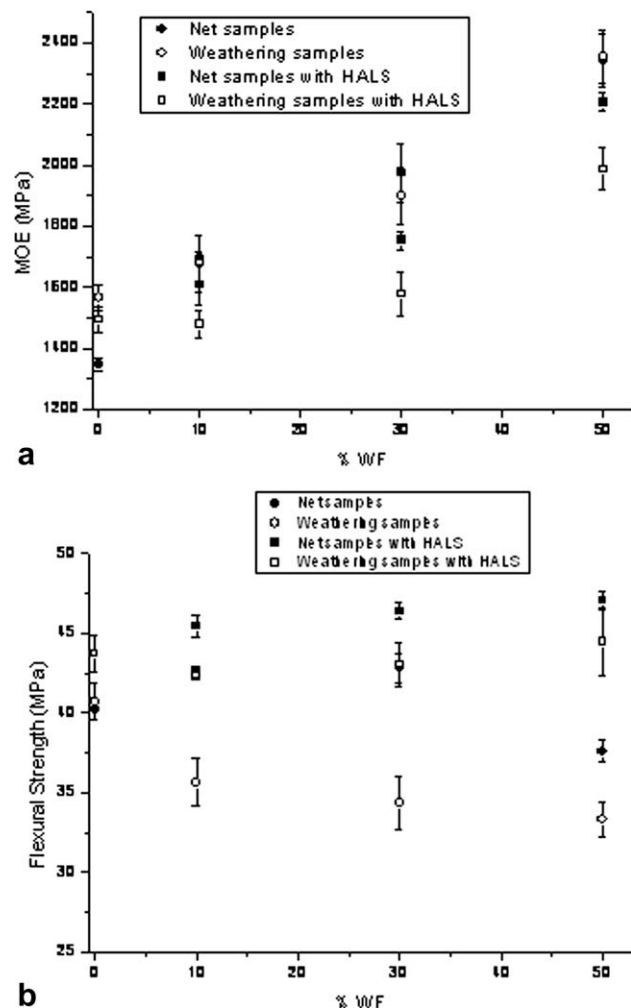To prevent the adverse effects produced for the Xenotest radiation, HALS and UV stabilizers were

Figure 5 Flexural modulus (a) and flexural strength (b) for the neat samples and weathered samples with and without HALS.
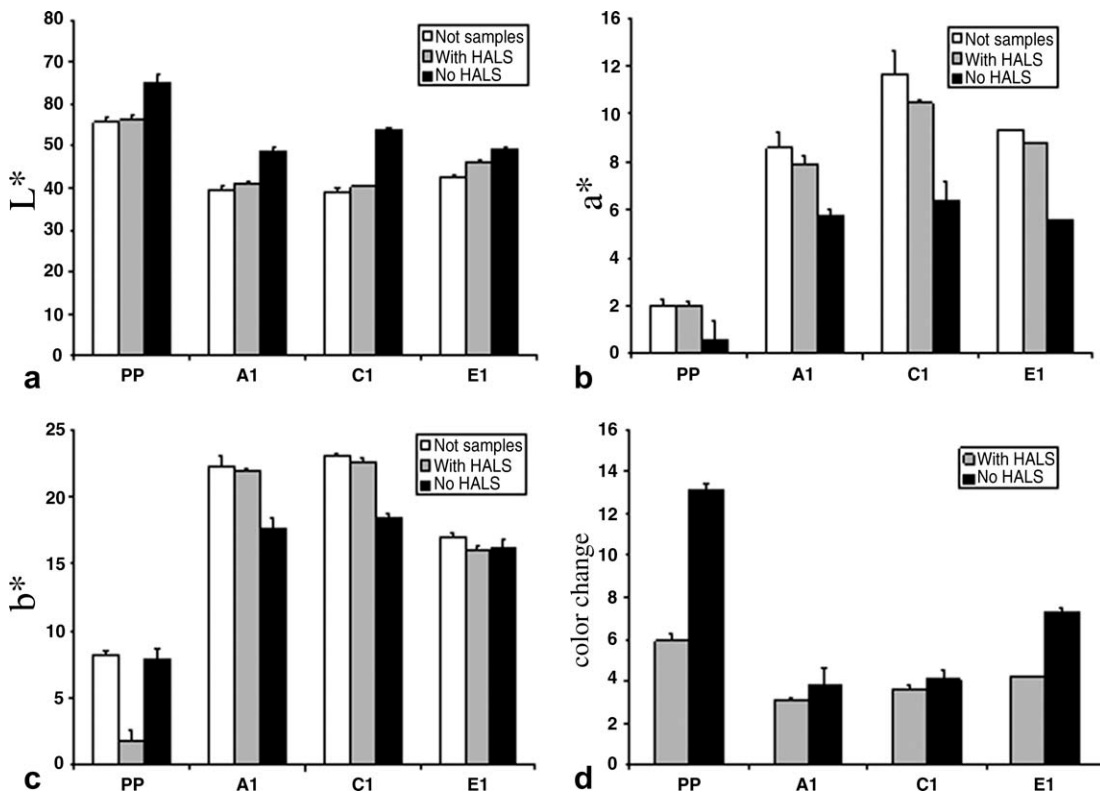
Figure 6 Color measurements: lightness (a), chromaticity $a*$ (b), chromaticity $b*$ (c), and color change (d).
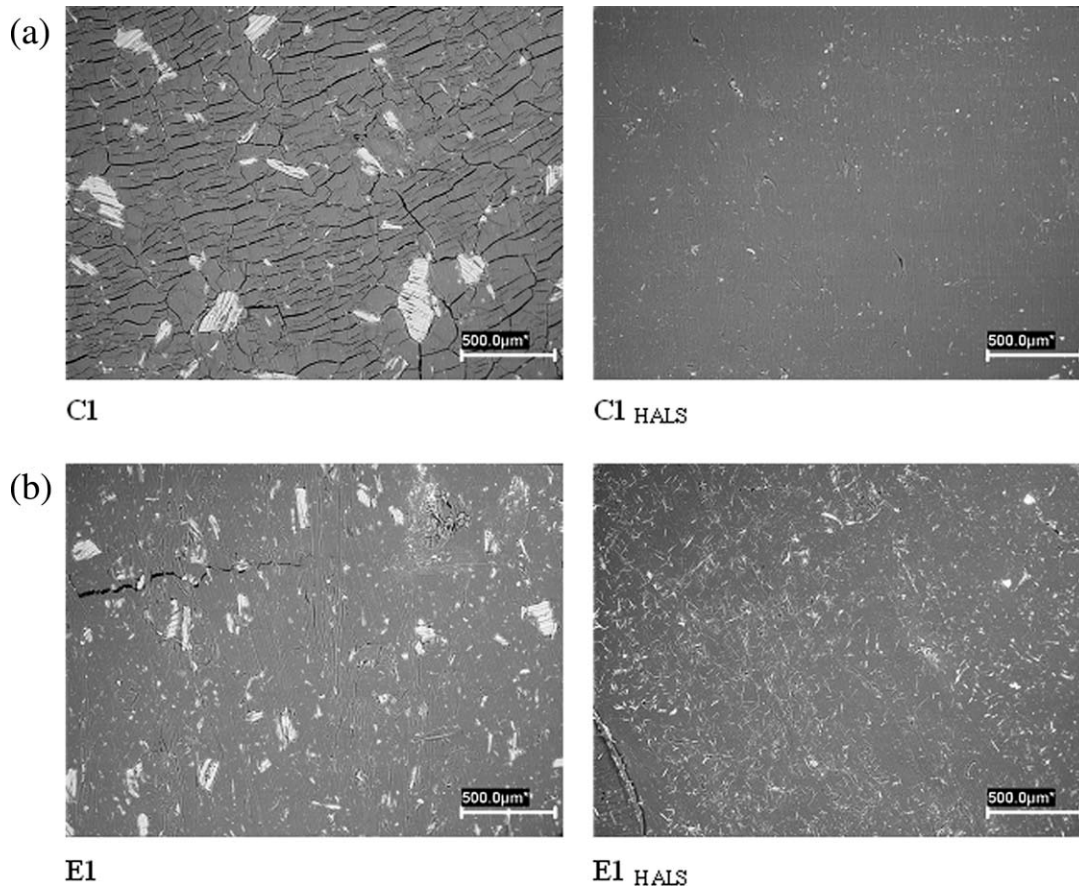

Figure 7 SEM micrographs surface blends after weathering of (a) C1 and C1$_{HALS}$, (b) E1 and E1$_{HALS}$ samples.
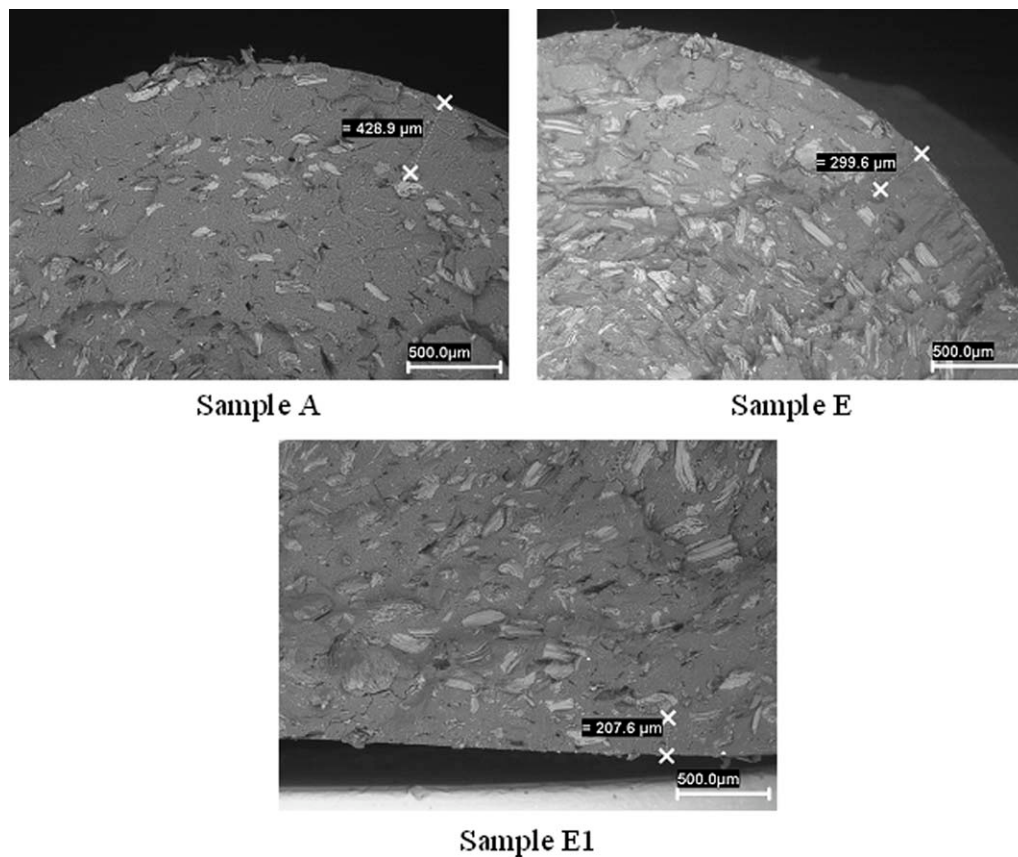
Figure 8 SEM micrographs showing the skin-core effect in samples A, E, and E1.

added to selected samples. These samples were characterized by both their mechanical properties and the surface analysis.

The analysis of the flexural properties shows that HALS addition to the polypropylene matrix produces a decrease in the value of flexural modulus [Fig. 5(a)]. Because HALS contain a diester in their molecular structure, the carbonyl groups present are susceptible to thermo-oxidative degradation during the extrusion process. This implies the division of polymer chains that leads to a loss of material stiffness. As seen earlier, the flexural modulus of samples that have not undergone radiation exposure increases with woodflour content. However, after the aging, these values fall slightly.

The addition of stabilizers implies a slight decrease in flexural modulus when compared with samples that do not contain any. However, the addition of HALS photostabilizers does not prevent completely the loss of rigidity of composite materials after the accelerated aging.

The flexural strength values before and after radiation exposure, are shown in Figure 5(b). Xenotest radiation exposure produces a drop in flexural strength values [Fig. 5(b)]. However, this reduction is much greater in samples that do not contain HALS (~ 6 MPa). In samples with HALS, flexural strength

remains constant after degradation. In short, samples containing HALS in its formulation reach higher strength values, possibly because these compounds can undergo reactions in the interface that increase material resistance. However, the specific reaction mechanism is not completely defined.

Surface analysis: Color measurement and scanning electron microscopy

Lightness is the sum of the reflectance from a sample (total area under the spectral/curve) and is independent of shade sample. The lightness of composites is mainly due to the whitening of the material that can be attributed mainly to wood.

The lightness (L^*) measurements of polypropylene and composites are presented in Figure 6(a). This figure shows the values for samples with and without photostabilizers (UV absorbers and HALS), before and after aging.

The lightness of polypropylene and composites that do not contain photostabilizers increases after the aging radiation. In general, the color of WPCs lightens during weathering.[22] These results are consistent with those obtained by other authors in composites of high-density polyethylene/wood[19] and PP-wood mixtures.[23]

As for chromaticity coordinates a^* b^* [Fig. 6(b–c)], as a general rule, the exposure of composite materials to radiation implies a decline in chromaticity a^* [Fig. 6(b)]. A decrease in chromaticity b^* was also observed. Moreover, the incorporation of the photostabilizers into composite materials effectively prevents the loss of a^* and b^*.

The color change [Fig. 6(d)] is higher in samples that do not contain photostabilizers. Thus, the superficial aspect of the samples tested once have undergone radiation and is maintained when stabilizers are added to the formulations. The biggest color change occurs in the PP, followed by the sample E1, where the content of wood is greater, and therefore, bleaching is also produced.

To estimate the effects of HALS on the composite properties, the micrographs of the surfaces of injection-molded composites after weathering with and without HALS are shown in Figure 7. The photodegradation of PP causes surface cracking and cracks appeared on the surface of C1 and E1 composites. The stabilization of the matrix with the antioxidants and UV stabilizers inhibited surface cracking during weathering. With HALS addition, the surface is relatively smoother and there are not cracks on the surface. Moreover, the WF particles rose from the surface in sample E1. Addition of HALS did not prevent this occurrence, but rather reduced it.

Other causes may also be considered; the manufacturing method used directly influences composite surface characteristics. Stark et al. have demonstrated that WPCs with similar formulations manufactured differently, using injection molding or extrusion, influenced the rate of lightening.[17,48] Injection-molded composites lightened more slowly upon weathering than extruded composites due to a hydrophobic PP layer that formed on the composite surface during injection molding. A skin-core effect can be observed in Figure 8. As we can see, skin thickness (rich in PP matrix) decreases with the WF amount of the composite. However, for similar PP/woodflour compositions, the skin is thinner for the composites with silane-treated filler due to the increment in matrix–filler compatibility. Stark obtained similar results in HDPE/WF samples.[45]

CONCLUSIONS

The principal conclusions of this study on the effects of moisture absorption and weathering on the physical properties of woodflour composites are summarized as follows:

Although, the moisture uptake of materials is proportional to the wood content, silane incorporation decreases the accessibility of water molecules to reactive regions, and the moisture absorbed is reduced by more than half-fold.

In wet samples, there is a marked reduction in the storage modulus in the glass and rubber zone measured by dynamic mechanical analysis, since water has a plasticizer effect associated with a diminution in the T_g of the materials.

With respect to the flexural properties, the moisture deteriorates the interfacial adhesion between filler and matrix, and consequently, the mechanical properties of the composites. The WPCs processed with woodflour treated with 1% vinyltrimethoxysilane are less susceptible to water absorption in moist environments and thus better maintain the original macroscopic properties of the composite materials.

With respect to weathering, HALS maintains the brightness of the materials after the aging and prevents the whitening of the samples. Furthermore, the additives reduce the loss of color after aging.

Although the slight decrease in the mechanical properties was not avoided, the combination of the additives studied (UV absorbers and/or HALS) successfully prevented the deterioration of surface materials by UV radiation.

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